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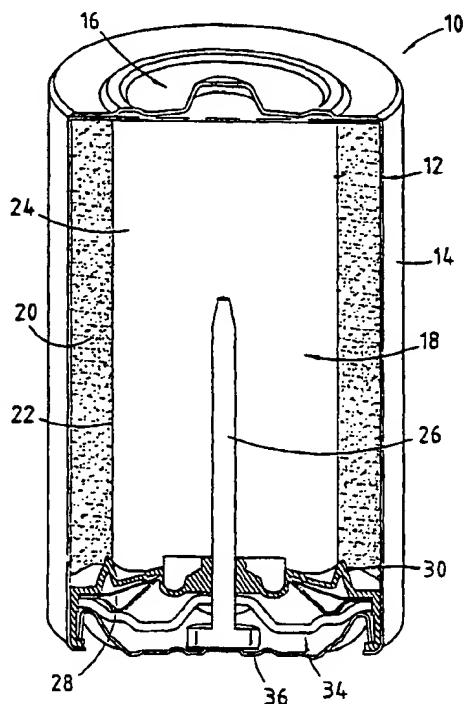
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(54) Title: ALKALINE ELECTROCHEMICAL CELL HAVING AN ANODE ADDITIVE



(57) Abstract: An electrochemical cell is provided that comprises a cathode, an alkaline electrolyte, and an anode with a sulfide, phosphate, or carbonate additive. Also provided is a method of making an electrochemical cell comprising the steps of providing a cathode, an electrolyte, and an anode, adding a sulfide, phosphate, or carbonate additive to the anode, and putting the anode and cathode in contact with the electrolyte. The additive can lead to improved discharge performance of the anode, and increased discharge capacity.

WO 01/41237 A1

ALKALINE ELECTROCHEMICAL CELL HAVING AN ANODE ADDITIVE

5 The present invention relates generally to electrochemical cells having anode additives, and more particularly to anode additives that boost zinc anode high rate discharge performance in an alkaline cell.

10 Conventional alkaline cells generally include a steel cylindrical can having a cathode comprising manganese dioxide as the active material and formed on the interior surface of the steel can, an anode comprising zinc powder as the active material and located in the centre of the cell, a separator located between the anode and the cathode, and an alkaline electrolyte solution simultaneously contacting the anode, the cathode, and the separator. A conductive current collector is commonly inserted into the anode
15 active material and a seal assembly provides closure to the top end of the steel can.

 A goal in designing alkaline battery cells is to increase the anode discharge performance at high rate. The zinc discharge efficiency is generally low at a high rate of discharge. The cause for the low zinc utilisation and discharge efficiency may be due to
20 the reaction products in the cell at high rate discharge which block or passivate the zinc surfaces. The reaction products are believed to be voluminous, thus reducing the ion transport inside the cell.

 Electrochemical cell manufacturers and consumers desire an electrochemical cell
25 with better performance and, therefore, there is an ongoing need for better performing electrochemical cells that are low in cost.

 We have now found that the discharge service performance of an electrochemical cell can be surprisingly improved by the addition of a selected additive
30 to the anode of the cell.

Accordingly, in a first aspect, the present invention provides an electrochemical cell comprising an anode having anode active material and, as an anode additive, at least one compound selected from sulfide, phosphate and carbonate compounds.

5 In a second aspect, the present invention provides a method of constructing an electrochemical cell comprising the steps of providing a cathode, an alkaline electrolyte, and an anode, and adding to the anode, as an anode additive, at least one compound selected from sulfide, phosphate and carbonate compounds.

10 The present invention advantageously provides for enhanced discharge efficiency by employing an anode containing a sulfide additive, a phosphate additive, a carbonate additive, or a combination thereof. In an embodiment of the first aspect, an electrochemical cell is provided that comprises an alkaline electrolyte and an anode having a sulfide, or a phosphate, or a carbonate. In an embodiment of the second aspect,
15 a method of constructing an electrochemical cell is provided that comprises the steps of providing a cathode, an alkaline electrolyte, and an anode, and adding a sulfide, phosphate, or carbonate additive to the anode.

According to a first embodiment, the anode contains a sulfide compound,
20 preferably sodium sulfide (Na_2S). Another preferred sulfide additive is potassium sulfide, K_2S_n , where n is either 1 or 2. Other sulfides, such as zinc sulfide, may also be employed. The sulfide compound additive is preferred to comprise from about 0.01
percent to about 0.75 percent by weight of the anode gel mix, the anode gel mix preferably being a zinc anode gel mix. The sulfide compound may comprise about 0.35
25 weight percentage of the anode gel mix, according to one example. In a preferred embodiment, an anode gel is prepared that contains 67 percent by weight zinc and 33 percent electrolyte (preferably a 37 percent solution of KOH) and gelling agent. Na_2S is
added to the zinc anode in an amount of 0.35 percent by weight of the anode gel mix.

30 Advantageously, the discharge performance of an anode with the sulfide additive may be improved over that of a control anode that does not include the additive, and the

discharge capacity may be increased, for example by about 40 percent, compared to a control anode. Furthermore, the amount of gassing of an anode with the sulfide additive may be decreased, compared with a control anode that does not include the additive.

5 Other advantages to using a sulfide additive are that it is safe, easy, and convenient to handle in an alkaline electrolyte. No equipment, operation, or battery design needs to be changed to use the sulfide additive. Furthermore, the sulfide ion dissolves in a KOH electrolyte solution, which is the preferred way to add it to the cell of the present invention. Also, a sulfide can be introduced to the cell using a
10 variety of different cations.

 Therefore, in a preferred embodiment, a method of making an electrochemical cell is provided that comprises the steps of: providing a cathode; providing an alkaline electrolyte; providing an anode; adding a sulfide additive to said anode; and putting the
15 cathode and the anode in contact with the electrolyte.

 On discharge of cells that use an anode, such as a zinc anode, without an additive present in the anode, large particles of discharge product tend to form on the surface of the zinc anode. On the other hand, if a sulfide compound, such as sodium
20 sulfide (Na_2S), is included in the anode, the particles formed on the zinc surface are much smaller. Thus, the use of a sulfide additive leads to a decreased particle size for the discharged product. This is believed to increase the ability of ion flow from the zinc surface, thereby enhancing the discharge characteristics of the cell. It is believed that
25 phosphate and carbonate additives also lead to decreased particle size for the discharged product. Therefore, the anode additive is preferably such that discharge product formed on the anode active material, on discharge of the cell, is of a decreased particle size as compared with discharge product formed in the cell without the anode additive.

 According to a second embodiment, the anode contains an additive having a
30 phosphate ion (PO_4^{3-}). The phosphate compound is preferably added to the anode gel in an amount of from about 0.1 percent to about 2.0 percent by weight of the anode gel

mix. More preferably, the anode gel contains about 1.5 percent by weight of the phosphate compound.

Advantageously, passivation may be delayed in a zinc anode that contains the phosphate additive, and the zinc dissolution limiting current may be increased with the phosphate additive. Also, the discharge performance of an anode with the phosphate additive may be improved over that of a control anode that does not include the additive, and the discharge capacity may be increased, for example by about 15 percent, compared to a control anode. Furthermore, the amount of gassing of an anode with the phosphate additive may be decreased, compared with a control anode that does not include the additive.

Additional benefits of using a phosphate additive are that it is environmental friendly, easy to use, and convenient to handle. No equipment, operation, or battery design needs to be changed to use the phosphate additive in the zinc anode. The phosphate additive is preferably dry mixed with zinc powder prior to making the anode gel mix. The phosphate additive can also be dissolved in the KOH electrolyte. Furthermore, the phosphate additive can be used with a variety of different cations which makes it a very versatile anion to use as an additive to an electrochemical cell.

Therefore, in a preferred embodiment, a method of making an electrochemical cell is provided that comprises the steps of: providing a cathode; providing an alkaline electrolyte; providing an anode; adding a phosphate additive to the anode; and putting the cathode and the anode in contact with the electrolyte.

According to a third embodiment, the anode contains an additive having a carbonate ion (CO_3^{2-}), preferably potassium bicarbonate (KHCO_3). The amount of carbonate compound added to the anode is preferably from about 0.1 percent to about 2.0 percent by weight of the anode gel mix, and more preferably the anode gel mix contains about 0.5 percent of the carbonate compound by weight.

Advantageously, the discharge performance of an anode with the carbonate additive may be improved over that of a control anode that does not include the additive, and the discharge capacity may be increased, for example by about 12 percent, compared to a control anode.

5

Carbonate compounds are easy and convenient to handle and are safe. Furthermore, no equipment, operation, or battery design needs to be changed to use the carbonate additive, and carbonate can be introduced to the cell using a variety of different cations.

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Therefore, in a preferred embodiment, a method of making an electrochemical cell is provided that comprises the steps of: providing a cathode; providing an alkaline electrolyte; providing an anode; adding a carbonate additive to the anode; and putting the cathode and the anode in contact with the electrolyte.

15

The cell is preferably an alkaline electrochemical cell, and is preferably cylindrical, although other cell types and configurations may be used. The anode of the present invention preferably contains zinc powder as the electrochemically active material, and an additive as discussed in more detail below. For example, the anode may be formed of zinc powder, a gelling agent, and additive. The cathode of the present invention is preferably formed of electrolytic manganese dioxide (EMD) as the electrochemically active material. In addition, the cathode of the present invention may also contain one or more cathode additives. For example, the cathode may be formed of a mixture of manganese dioxide, graphite, a 45% potassium hydroxide solution, water, and an aqueous Teflon® solution comprising approximately 20% polytetrafluoroethylene, and additives. A separator is generally disposed between the anode and the cathode, and is preferably formed of a nonwoven fabric that prevents migration of any solid particles in the cell. The electrolyte is preferably an alkaline electrolyte, more preferably potassium hydroxide (KOH) aqueous solution. It is contemplated that other anodes, cathodes, electrolytes, and separators may be used in accordance with the present invention.

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The present invention will be further understood by reference to the embodiments shown in the drawings, in which:

Figure 1 is a cut away perspective view of an alkaline electrochemical cell that may employ an anode additive in accordance with the present invention;

5 Figure 2 is a graph comparing the discharge curves of a zinc anode without an additive and a zinc anode having a Na_2S additive;

Figure 3 is a graph comparing the anodic polarisation of a zinc anode without an additive and a zinc anode having a KH_2PO_4 additive;

10 Figure 4 is a graph comparing the discharge curves of a zinc anode without an additive and a zinc anode having a KH_2PO_4 additive;

Figure 5 is a graph comparing the discharge curves of a zinc anode without an additive and a zinc anode having a KHCO_3 additive;

Figure 6 is a photograph of a zinc anode at a magnification of 200x, where no additive was included in the anode;

15 Figure 7 is a photograph of a zinc anode at a magnification of 2000x, where no additive was included in the anode;

Figure 8 is a photograph of a zinc anode at a magnification of 200x, where Na_2S was added to the anode; and

20 Figure 9 is a photograph of a zinc anode at a magnification of 2000x, where Na_2S was added to the anode.

Referring to Figure 1, a cut away view of a cylindrical alkaline electrochemical cell 10 is shown. Alkaline cell 10 includes a steel can 12 having a cylindrical shape with a closed bottom end and an open top end. A metalised, plastic film label 14 is
25 formed about the exterior surface of steel can 12, except for the ends of steel can 12. At the closed end of steel can 12 is a positive cover 16 preferably formed of plated steel. Film label 14 is formed over the peripheral edge of positive cover 16. A cathode 20, preferably formed of a mixture of manganese dioxide, preferably electrolytic manganese dioxide (EMD), as the electrochemically active material, graphite, a 45% potassium
30 hydroxide solution, water, and an aqueous Teflon® solution comprising approximately 20% polytetrafluoroethylene, and one or more cathode additives, is formed about the

interior surface of steel can 12. A separator 22, which is preferably formed of a nonwoven fabric that prevents migration of any solid particles in the cell, is disposed about the interior surface of cathode 20. An alkaline electrolyte 24, preferably formed of potassium hydroxide (KOH), is disposed in the can 12, preferably within the interior of separator 22. An anode 18, preferably formed of zinc powder as electrochemically active material, a gelling agent, and additives as discussed below is disposed within electrolyte 24 in contact with a current collector 26, which may include a brass nail. Accordingly, cathode 20 is configured as the positive electrode of the cell and the anode 18 is configured as the negative electrode of the cell.

Current collector 26 contacts a brass rivet formed at the open end of steel can 12. A nylon seal 30 is formed at the open end of steel can 12 to prevent leakage of the active materials contained in steel can 12. Nylon seal 30 contacts a metal washer 28 and an inner cell cover 34, which is preferably formed of steel. A negative cover 36, which is preferably formed of plated steel, is disposed in contact with current collector 26 by a weld. Negative cover 36 is electrically insulated from steel can 12 by nylon seal 30.

Figure 2 shows the discharge curves of a zinc anode without an additive and a zinc anode having a sodium sulfide (Na_2S) additive. An anode gel is prepared that contains 67 percent by weight zinc and 33 percent electrolyte, preferably a 37 percent solution of KOH. Na_2S is added to the zinc anode in an amount of 0.35 percent by weight of the anode gel mix. The characteristics of a zinc anode "half cell" with 0.35 weight percent Na_2S based on total anode mix added were compared to that of a "control" zinc anode. The control anode is the same in all respects as the anode with Na_2S , except that the control contains no added sulfide. Figure 2 shows a comparison of discharge curves of two two-gram samples of pre-gelled zinc anodes, one mixed with Na_2S additive and one without, at a discharge rate of 250 mA/g in a flooded half cell. Line 40 shows the discharge characteristics of the half cell with the zinc "control" anode having no additive. Line 42 shows the discharge characteristics of a 67 weight percent zinc anode with a Na_2S additive at 250 mA/g in a flooded half cell. The results demonstrate that the discharge performance of the anode with the sulfide additive is an

improvement over that of the control anode and that the discharge capacity has been increased about 40 percent compared to the control zinc anode.

Table 1 below shows the straight shelf gassing results, comparing the zinc control anode versus the zinc anode with a Na_2S additive. The gassing test used a five-gram sample of zinc in a syringe at 71°C for 24 hours to measure the gassing effect of the anode. The results show that the zinc control anode gassed 0.062 ml/g/day, whereas the zinc anode with Na_2S gassed 0.054 ml/g/day.

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TABLE 1

Sample (5g)	#	V_{initial} (ml)	V_{final} (ml)	V_{diff} (ml)	Gassing (ml/g/day)
Zinc without Na_2S (Control)	1	3.86	4.19		
	2	3.99	4.25		
	3	3.84	4.18		
	Average	3.90	4.21	0.31	0.062
Zinc with 0.25 weight percent Na_2S	1	3.99	4.23		
	2	3.88	4.19		
	3	3.94	4.20		
	Average	3.94	4.21	0.27	0.054

Figure 3 shows the anodic polarisation of pressed zinc pellets with and without potassium diphosphate (KH_2PO_4) additive. Line 50 represents the polarisation of the anode with KH_2PO_4 added to a zinc anode, and line 52 shows the zinc "control" anode without additive. Figure 3 demonstrates that zinc passivation is delayed and that the zinc dissolution limiting current is increased with the phosphate additive.

Figure 4 compares the discharge curves of pre-gelled zinc anode mix with a KH_2PO_4 additive to the same zinc pre-gelled anode mix without the phosphate additive. The anode contains 1.5 percent by weight of a phosphate compound. The rate of discharge was 250 mA/g in a flooded half cell. Line 54 is the discharge curve for the pre-gelled zinc anode mix without additive, and line 56 is the discharge curve for the pre-gelled zinc anode mix with the phosphate additive. Figure 4 shows that the discharge performance has been improved and the discharge capacity has been increased about 15 percent by adding KH_2PO_4 to the pre-gelled zinc anode. In an experiment using five grams of zinc in a syringe test at 71°C for 24 hours, similar to that of the sulfide test, the zinc anode with the KH_2PO_4 showed less gassing than the zinc "control" anode without additive.

Figure 5 compares the discharge curves of pre-gelled zinc anode mix with a potassium carbonate (KHCO_3) additive to the same zinc pre-gelled anode mix without the carbonate additive. The anode gel mix contains 0.5 percent of the carbonate compound by weight. The rate of discharge was 250 mA/g in a flooded half cell. Line 60 is the discharge curve for the pre-gelled anode mix without additive, and line 62 is the discharge curve for the pre-gelled anode mix with the carbonate additive. Figure 5 shows that the discharge performance has been improved and the discharge capacity has been increased about 12 percent by adding KHCO_3 to the pre-gelled zinc anode.

Figures 6 to 9 demonstrate that the use of an additive leads to decreased particle size for the discharged product. Figures 6 and 7 show a magnified photo of the surface features of the anode after discharge where no additive was present in the anode. In Figures 6 and 7, it can be seen that large particles form on the surface of the zinc anode

when no sulfide, carbonate or phosphate additive is present in the anode. On the other hand, in Figures 8 and 9, where a 0.05 weight percent Na_2S additive was included in the anode, the particles formed on the zinc surface are much smaller.

CLAIMS:

1. An electrochemical cell comprising an anode having anode active material and,
5 as an anode additive, at least one compound selected from sulfide, phosphate and carbonate compounds.
2. A cell according to claim 1, wherein the anode additive comprises a sulfide compound.
10
3. A cell according to claim 2, wherein the sulfide compound is sodium sulfide (Na_2S).
4. A cell according to claim 2, wherein the sulfide compound is selected from zinc
15 sulfide (ZnS) and potassium sulfide (K_2S_n , where $n = 1$ or 2).
5. A cell according to any of claims 2 to 4, wherein the anode comprises from about 0.01 percent to about 0.75 percent sulfide compound, by weight of the anode.
- 20 6. A cell according to claim 5, wherein the anode comprises about 0.05 percent sulfide compound, by weight of the anode.
7. A cell according to claim 1, wherein the anode additive comprises a phosphate compound.
25
8. A cell according to claim 7, wherein the phosphate compound is potassium diphosphate (KH_2PO_4).
9. A cell according to claim 7 or claim 8, wherein the anode comprises from about
30 0.1 percent to about 2.0 percent phosphate compound, by weight of the anode.

10. A cell according to claim 9, wherein the anode comprises about 0.5 percent to about 1.5 percent phosphate compound, by weight of the anode.
11. A cell according to claim 1, wherein the anode additive comprises a carbonate compound.
12. A cell according to claim 11, wherein the carbonate compound is potassium bicarbonate (KHCO_3).
13. A cell according to claim 11 or claim 12, wherein the anode comprises from about 0.1 percent to about 2.0 percent carbonate compound, by weight of the anode.
14. A cell according to claim 13, wherein the anode comprises about 0.5 percent carbonate compound, by weight of the anode.
15. A cell according to any preceding claim, wherein the anode active material comprises zinc.
16. A cell according to any preceding claim, wherein the cell comprises an alkaline electrolyte.
17. A cell according to any preceding claim, wherein the anode additive is such that discharge product formed on the anode active material, on discharge of the cell, is of a decreased particle size as compared with discharge product formed in the cell without the anode additive.
18. A method of constructing an electrochemical cell comprising the steps of providing a cathode, an alkaline electrolyte, and an anode, and adding to the anode, as an anode additive, at least one compound selected from sulfide, phosphate and carbonate compounds.

19. A method according to claim 18, wherein the anode comprises zinc as anode active material.

20. A cell according to claim 18 or claim 19, wherein the anode additive is such that
5 discharge product formed on the anode active material, on discharge of the cell, is of a decreased particle size as compared with discharge product formed in the cell without the anode additive.

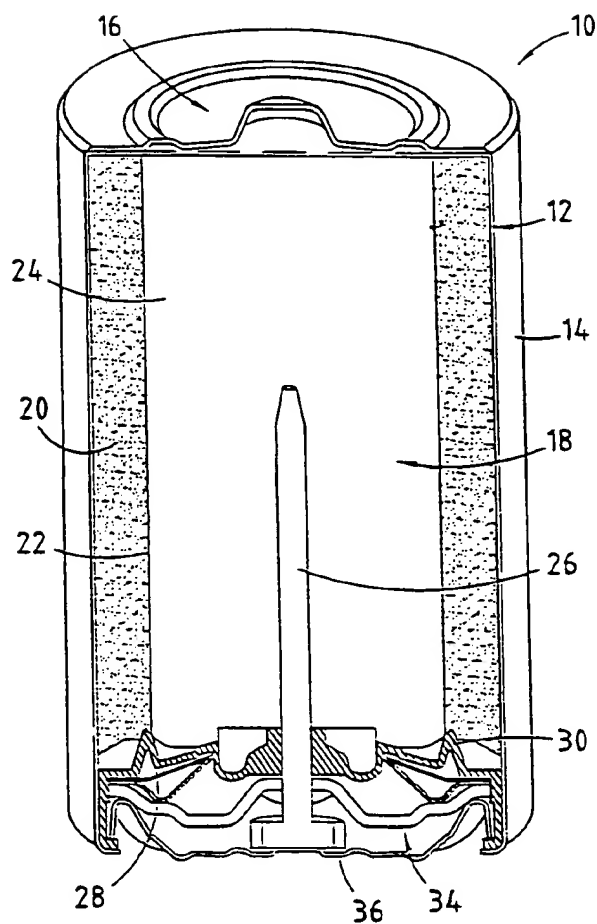
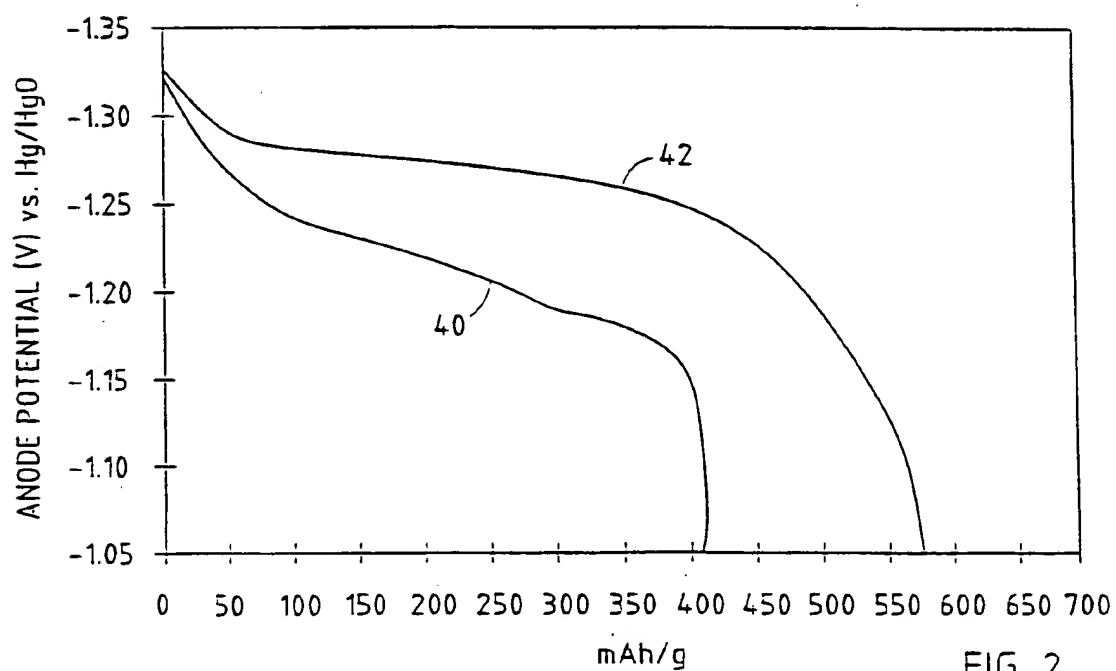


FIG. 1



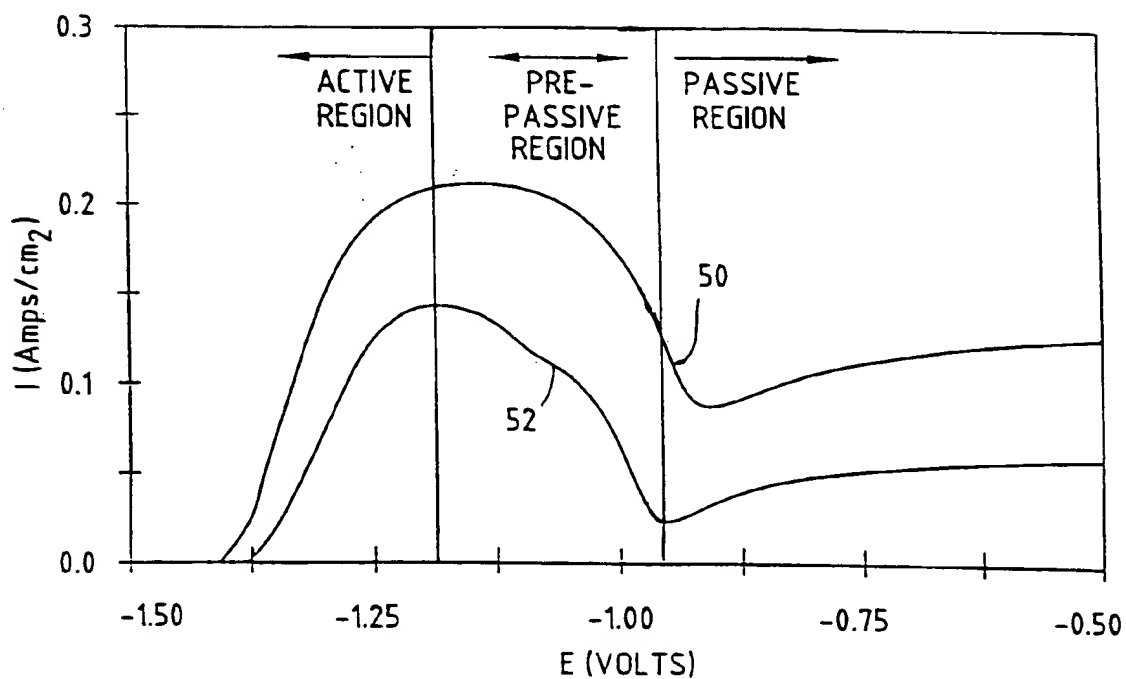


FIG. 3

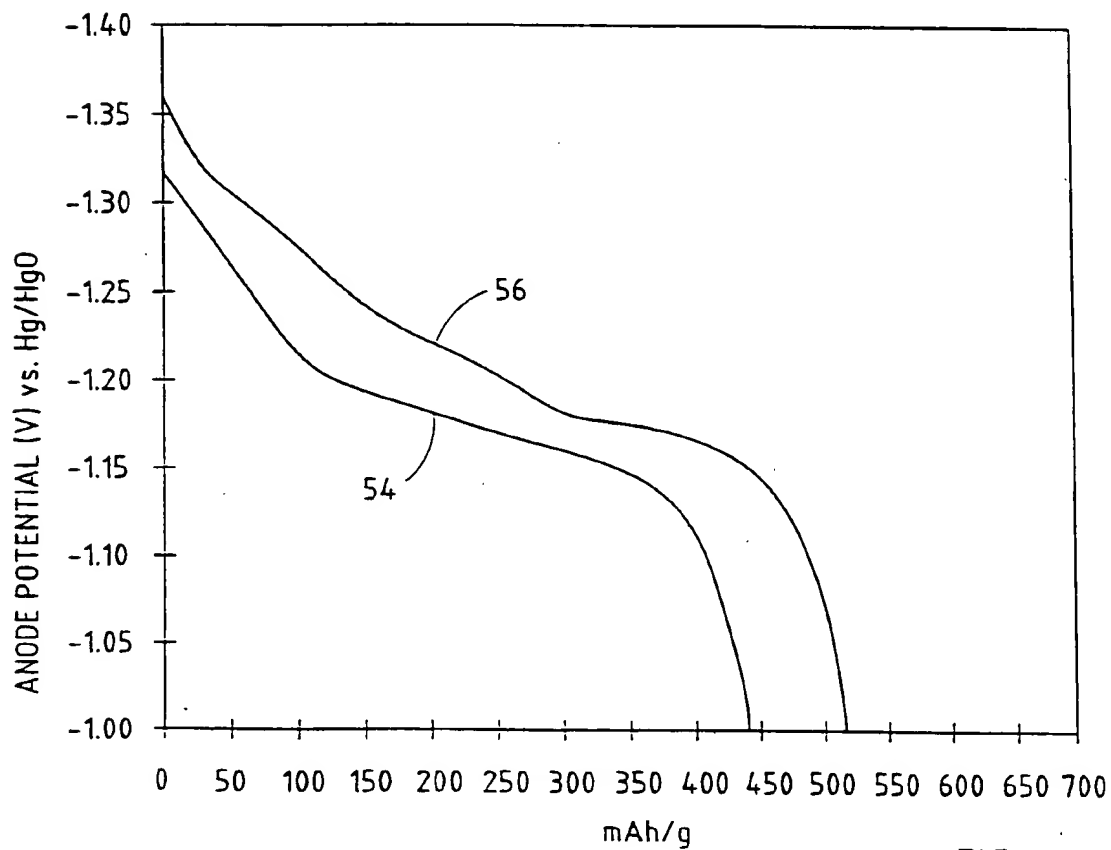


FIG. 4

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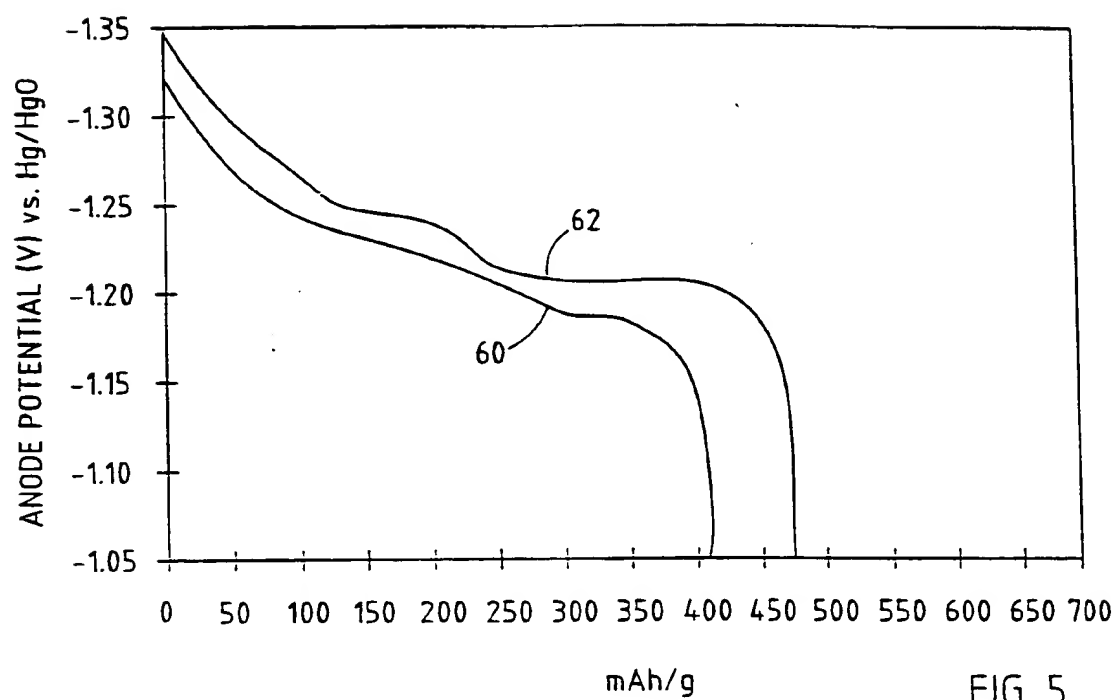
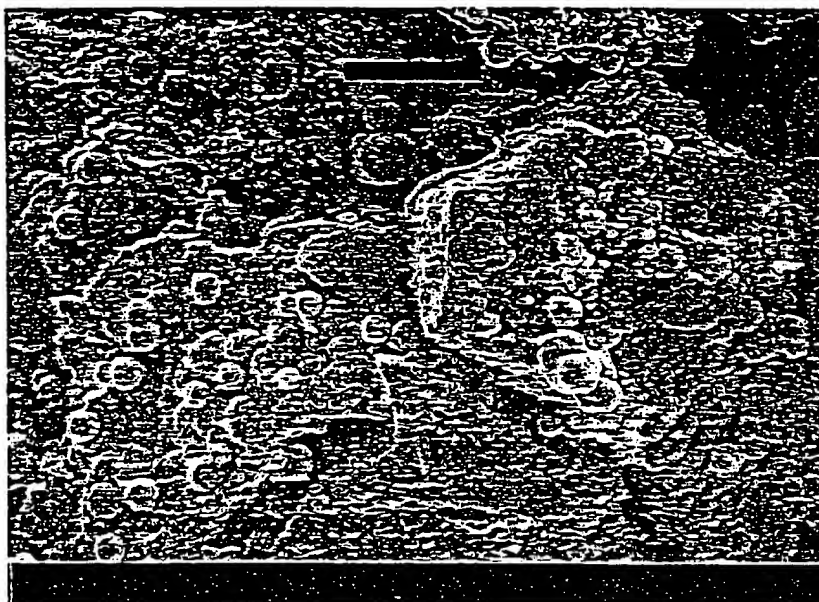


FIG. 5



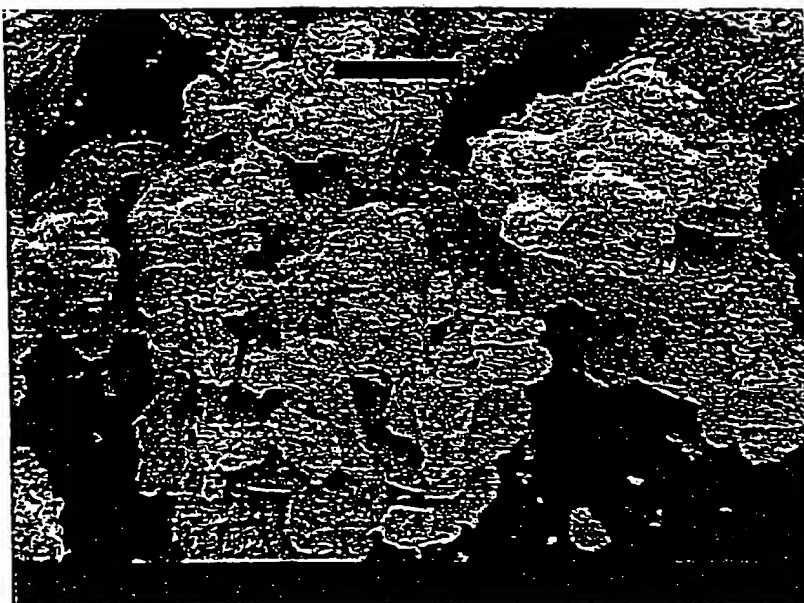
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FIG. 6



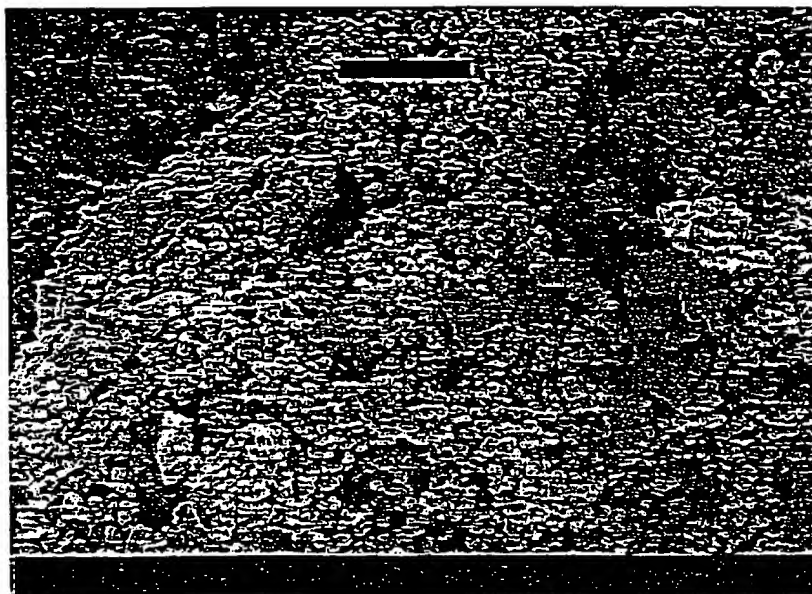
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FIG. 7



200 x

FIG. 8



2000 x

FIG. 9

PCT/US 00/32824

INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 840 644 A (CHALILPOYIL PURUSH ET AL) 20 June 1989 (1989-06-20) column 1, line 8 - line 11 column 2, line 24 - line 61 column 3, line 38 - line 50 example 1 claim 1 ---	1,7,9,10
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 11, 30 September 1999 (1999-09-30) -& JP 11 154535 A (SHIN KOBE ELECTRIC MACH CO LTD), 8 June 1999 (1999-06-08) abstract ---	1,7
A		8-10,18
A	BALASUBRAMANIAN T S ET AL: "EFFECT OF METAL-SULFIDE ADDITIVES ON CHARGE/DISCHARGE REACTIONS OF THE ALKALINE IRON ELECTRODE" JOURNAL OF POWER SOURCES,CH,ELSEVIER SEQUOIA S.A. LAUSANNE, vol. 41, no. 1/02, 5 January 1993 (1993-01-05), pages 99-105, XP000396204 ISSN: 0378-7753 page 100, line 11 - line 22 -----	1,2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/32824

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0206202 A	30-12-1986	FR 2583580 A	19-12-1986
		AT 45249 T	15-08-1989
		AU 583924 B	11-05-1989
		AU 5872086 A	24-12-1986
		CN 86104755 A	27-05-1987
		DE 3664845 D	07-09-1989
		DK 283286 A	19-12-1986
		IL 79123 A	28-09-1989
		JP 2001695 C	20-12-1995
		JP 7036330 B	19-04-1995
		JP 61292853 A	23-12-1986
		JP 2525719 B	21-08-1996
		JP 6187995 A	08-07-1994
		OA 8346 A	29-02-1988
		US 4781999 A	01-11-1988
US 3639176 A	01-02-1972	NONE	
US 4840644 A	20-06-1989	NONE	
JP 11154535 A	08-06-1999	NONE	